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Soojung Clara Leem

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Tetrathiafulvalene as a molecular building block in various systems

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Tetrathiafulvalene as a molecular building block in various systems

by

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Abstract

Tetrathiafulvalene as a molecular building block in various systems

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The University of Texas at Austin, 2015

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Tetrathiafulvalene (TTF), a classic electron rich donor system, has received renewed attention within the supramolecular and complex ligand chemical communities. As the result of recent synthetic advances, TTF and its derivatives have been incorporated into many complex receptor systems that have been explored as binding agents, sensors, and electron transfer models. In this thesis, the synthesis and the attempted use of TTF moieties in the construction of systems that could see a variety of applications will be described.

In the first chapter, a brief overview of the theoretical and historical background of TTF is given with the focus on the redox properties of TTF. The second chapter details the design of, and synthetic attempts to prepare a new TTF-based anion receptor. This latter system was designed to allow a well-recognized anion binding motif to be attached to a TTF core. However, the desired target was not obtained. The third chapter describes the author's contribution to the development of a self-assembled system comprised of a

TTF-substituted macrocycle and a functionalized fullerene. In this ensemble, two heteroditopic monomers combine to create a chemically and electrochemically responsive supramolecular oligomeric product.

Table of Contents

List of Figures

List of Schemes

Chapter 1: Introduction and Historical Overview of Tetrathiafulvalene

Although its derivatives containing dibenzene-, dimethyl- and biphenyl groups were synthesized several decades earlier,[1] unsubstituted tetrathiafulvalene (TTF) was only first synthesized in 1970 by Wudl.[2] TTF very soon began to attract considerable amount of attention as an electron donor with desirable redox properties, as detailed in early reports from Coffen et al.[3] and Hunig et al.[4] Furthermore, the discovery of the radical cation TTF ($TTF^{\cdot+}$) and its ion pair with chloride,[5] as well as the charge-transfer complex of TTF and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ),[6] initiated a fierce investigation of TTF as a component of electrically conducting materials. From this, the field of molecular electronics based on TTF, including the first superconducting organic material,[7] was developed.

One of the key characteristics of TTF is that it can undergo two reversible redox processes to produce $TTF^{\cdot+}$ and TTF^{2+} as shown below in Figure 1.1. Neutral TTF and its simple derivatives can be easily oxidized due to their low $E^1_{1/2}$ (0.34 V vs Ag/AgCl in acetonitrile for TTF) and $E^2_{1/2}$ (0.78 V vs Ag/AgCl in acetonitrile for TTF) values, These oxidation steps can be carried under either chemical or electrochemical conditions.

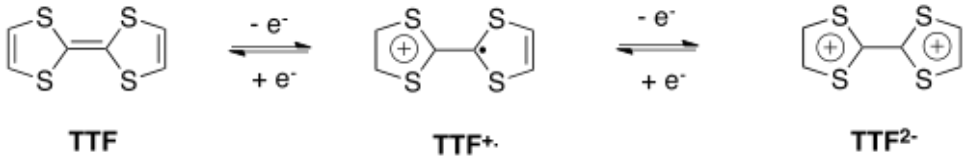


Figure 1.1: Reversible oxidations of TTF to the corresponding radical cation and dication species.

A neutral TTF molecule contains 14 π-electrons and displays non-aromatic characteristic. On the other hand, both of the oxidized species show aromatic character and contain either one ($TTF^{\cdot+}$) or two (TTF^{2+}) 6 π-electron 1,3-dithiolium cations within the overall structure. In addition to the putative aromatic stabilization present in the cationic forms, TTF contains multiple polarizable sulfur atoms. This serves to reduce the energy of the oxidized species. As a consequence, both oxidized species are thermodynamically stable. In fact, both one-electron oxidations are reversible. As a consequence of this reversibility, various interactions between molecules can be modulated by the successive transformation of TTF into its oxidized species or vice versa. This is a particularly effective approach when there are multiple TTF moieties present within a supramolecular complex or assembly. Such modulations can not only increase or decrease the extent of between the TTF subunits and a guest but also only the repulsion or the attraction of subunits but also induce global conformational changes throughout the entire system.

Other properties of TTF and its derivatives makes them attractive as molecular building blocks. In fact, TTF subunits have been used to construct molecular, supramolecular and macromolecular systems which respond to external stimuli. The

redox potential of TTF and its derivatives are also environmentally dependent. This allows TTF-containing systems to function as redox-responsive ligands. Moreover, TTF and TTF-bearing subunits show high propensity to undergo stacking, presumably as the result their small, planar geometry. Again, the resulting nanostructures be modulated by controlling the oxidation states of the incorporated TTF moieties.

Oxidation of TTF and its derivatives allows the electron donating ability of TTF-containing systems to be tuned. As a strong π-electron donor, TTF and its derivatives are capable of interacting with electron acceptors to form donor-acceptor units. The spectral properties of such donor-acceptor units containing TTF moieties can be modulated by switching the intermolecular charge transfer processes on or off. Photo-induced electron transfer processes within the assemblies can likewise be adjusted by reducing and oxidizing TTF subunits. The ability of TTF moieties to function as π-electron donors also plays an important role in dictating the extent to which TTF-containing compounds self-assemble. This subtle chemistry relies on π-π interactions, along with the interactions among sulfur atoms present within the molecules.[8]

A tremendous number of switchable molecular and supramolecular systems have been developed that take advantage of the three redox-states displayed by TTF derivatives. Many of these have seen use as molecular sensors, redox-fluorescent switches, electrochemically driven conformational controls and molecular clips and tweezers. In this thesis, the design, but ultimately unsuccessful synthesis of a potential dual-signaling anion receptor as well as the construction of a multi-input logic gate system using TTF derivatives will be described.

Chapter 2: A New Approach To A Potential Dual Signaling Anion Sensor: Tetrathiafulvalene-Indole Conjugate

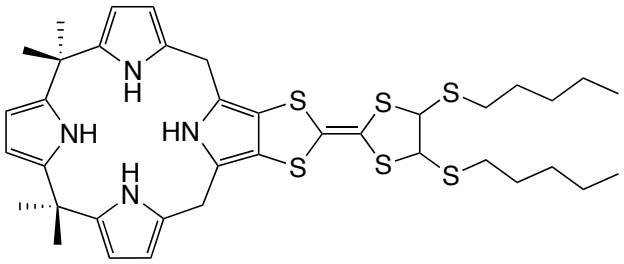
2.1 INTRODUCTION

2.1.1 Tetrathiafulvalene Derivatives as Anion Receptors

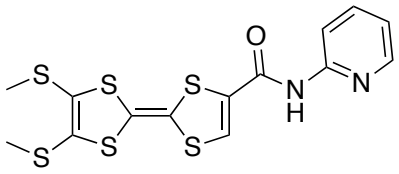
Tetrathiafulvalene (TTF) has been extensively exploited to construct redox-responsive electron-rich receptors that may be switched from one form to another as the result of the redox- and electron-donating properties of the TTF moiety. Upon the introduction of a guest, modulations in the redox and/or optical properties of the TTF subunits often occurs. This can produce an easy-to-monitor signal. TTF derivatives may also be attached to subunits that recognize neutral or ionic guest to give electroactive, stimuli-responsive systems. The incorporation of TTF derivatives into a system may permit full control over the binding behavior in addition to simple sensing. However, this paradigm is often difficult to implement as a result of the associated synthetic challenges with preparing the targeted compounds.[1]

Although tetrathiafulvalene has been extensively exploited both as a switching unit and as a supramolecular signaling unit, only very recently has it been incorporated into anion receptors. This may be also due to that the development of anion sensors has been investigated only in the past decade or so in spite of the important roles that anions play in chemical and biological processes. An initial report of an anion sensor based on TTF came from was made by Becher and coworkers. In 2003, they described the mono-TTF-

calix[4]pyrrole **2.1**. This system gives rise to an electrochemical signal upon the binding of the guest. This chemosensor was by annulating synthetically a redox-active TTF moiety onto a calix[4]pyrrole subunit. Calix[4]pyrrole was chosen since it was well known for its ability to recognize halide anions in organic media.[2] Zhu and coworkers also reported the combination of a TTF with an anion binding moiety in 2005. Their system, the neutral chemosensor **2.2**, is a hybrid of TTF and an aromatic amide-based platform. It was found to recognize selectively phosphate anions in methylene chloride. This phosphate anion binding gave rise to an electrochemical signal.[3]



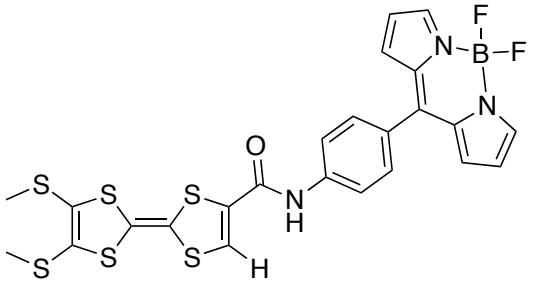
2.1



2.2

Subsequently, several TTF-based receptors were designed for the fluoride anion. This anion is a target of interest due to the diverse roles it plays in many biological, medical, and technological processes.[4] In 2011, You and coworkers reported a boron-dipyrromethane (BODIPY)-fused TTF derivative (**2.3**). They showed that this system acts as a sensor for the fluoride ion in a mixture of dimethylsulfoxide (DMSO) and water, giving rise to both an optical and electrochemical response.[5] Another chemosensor, which contains a TTF moiety as redox-active site and a dipyrrolyl motif as an anion recognition site is system **2.4**, which was reported by Langford and coworkers in 2012. Although this

latter receptor showed selective optical signaling, it did not produce the hoped-for electrochemical response upon exposure to the fluoride anion in methylene chloride.[6]



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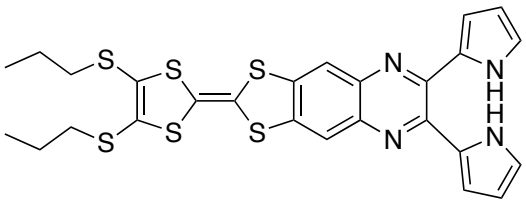
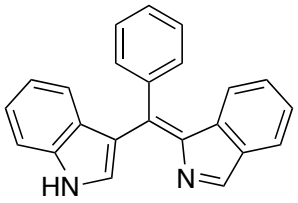


2.4

2.1.2 Use of Indole Moieties for the Sensing of Anions

Many systems that include neutral anion receptors containing hydrogen bond donors in acylic or macrocyclic frameworks have been reported recently. One subunitused to produce such receptors is indole. Indole contains a single N-H hydrogen bond donor and typically is a better hydrogen bond donor than simple pyrrole. This difference is reflected in the relative pKa values. That for pyrrole in DMSO is 23.0, whereas that for indole in DMSO is 21.0. However, it is also more prone to deprotonation, and this needs to be taken into consideration when designing anion receptors containing indole moieties.[7]

Classic indole based anion receptors are the bis(indolyl)methane **2.5** reported by Shao and coworkers[8] and the phenylhydrazone-functionalized indole **2.6** reported by Lin and coworkers[9]. Both gave rise to a change in the optical features upon exposure to the fluoride anion in acetonitrle (**2.5**) or DMSO (**2.6**). This response is ascribed to deprotonation of the indole N-H proton.



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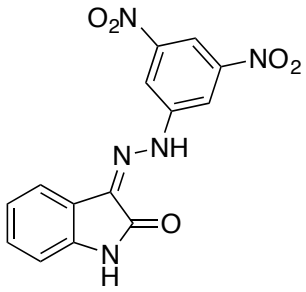
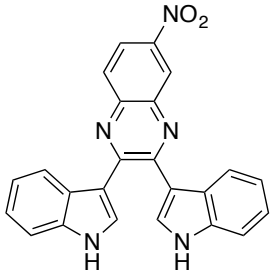


2.6

Selective anion receptors using diindolyl moieties also have been developed by many research groups. A diindolyquinoxaline derivative **2.7** was synthesized as a selective dihydrogen phosphate anion receptor by Sessler and coworkers. The binding of this target anion triggered color change, and this allowed visual detection of dihydrogen phosphate anion in dichloromethane.[10] The oxidation of **2.7** lead to receptor **2.8**, which demonstrated high affinity for the fluoride and acetate anions in DMSO.[11] Likewise, fusing **2.7** to a TTF moiety lead to a new receptor **2.9** with dual signaling capability. Exposure of this receptor to the dihydrogen phosphate anions in dichloromethane lead to quenching of the fluorescence (arising initially from the quinoxaline moiety), as well as producing an electrochemical readout that was reflected in a change in both the intensity and position of the reduction waves.[12]



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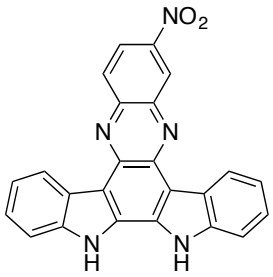

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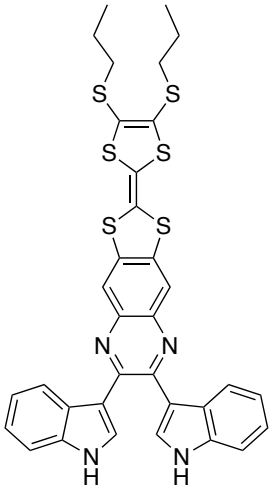
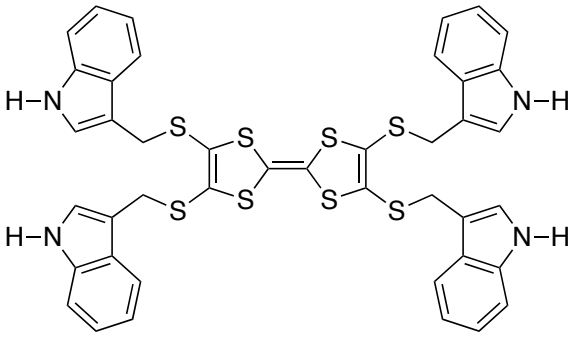


2.9

2.2 Design of the Receptor

Although indole is a longstanding anion recognition moiety, there are only few reports that describe its use in conjunction with an electrochemically signaling unit such as TTF. In fact, to our knowledge the only systems are the indole-TTF and quinoxaline systems noted in the previous section. We are unaware of any receptor system where an indole subunit is attached to a TTF core. To address this deficiency, a new receptor **2.10** was designed. This new receptor was an attractive target because it would contain indole subunits that are linked to a central TTF core through alkyl **2.10** tethers.

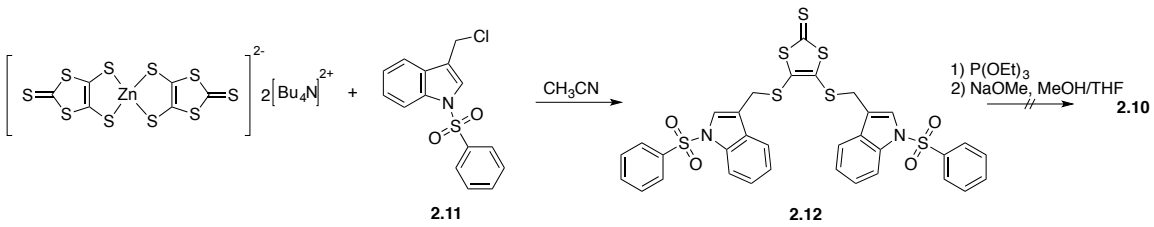


2.10

2.3 Synthesis of the Designed Receptor

The attempted synthesis of **2.10** is outlined in Scheme 2.1. Intermediate **2.11** was

prepared using a modification of reaction conditions described in the literature.[13] It was then reacted with the commercially available thiolate zinc complex to produce **2.12**. Intermediate **2.12** was characterized with ^{1}H NMR and ^{13}C NMR spectroscopy and high-resolution ESI mass spectrometry. Unfortunately, the phosphorus-mediated coupling of **2.12** and the subsequent deprotection by sodium methoxide did not proceed as expected.



Scheme 2.1: Attempted synthesis of **2.10**.

To identify the major species present in the crude reaction mixture and to obtain insights into the reasons of failure, mass spectrometry and high performance liquid chromatography (HPLC) were attempted. However, mass spectrometry revealed a spectrum with multiple peaks; HPLC could not be performed due to the poor solubility of the crude sample in any solvent suitable for HPLC.

On the other hand, the ^{1}H NMR and ^{13}C NMR spectra of the crude sample showed peaks that may correspond to an indole moiety being present. Furthermore, changes in the signal that could be from the indole N-H proton were monitored upon the exposure of the crude sample to various anions. The observed shift of peaks was similar to what was reported for **2.9**.[12] From the combined data, it can be suggested that a fragment of desired product containing indole moiety may be present in the crude product sample. If so, the

observed fragmentation could be due to harsh condition of coupling reaction (which involved heating at reflux 130ºC for many hours).

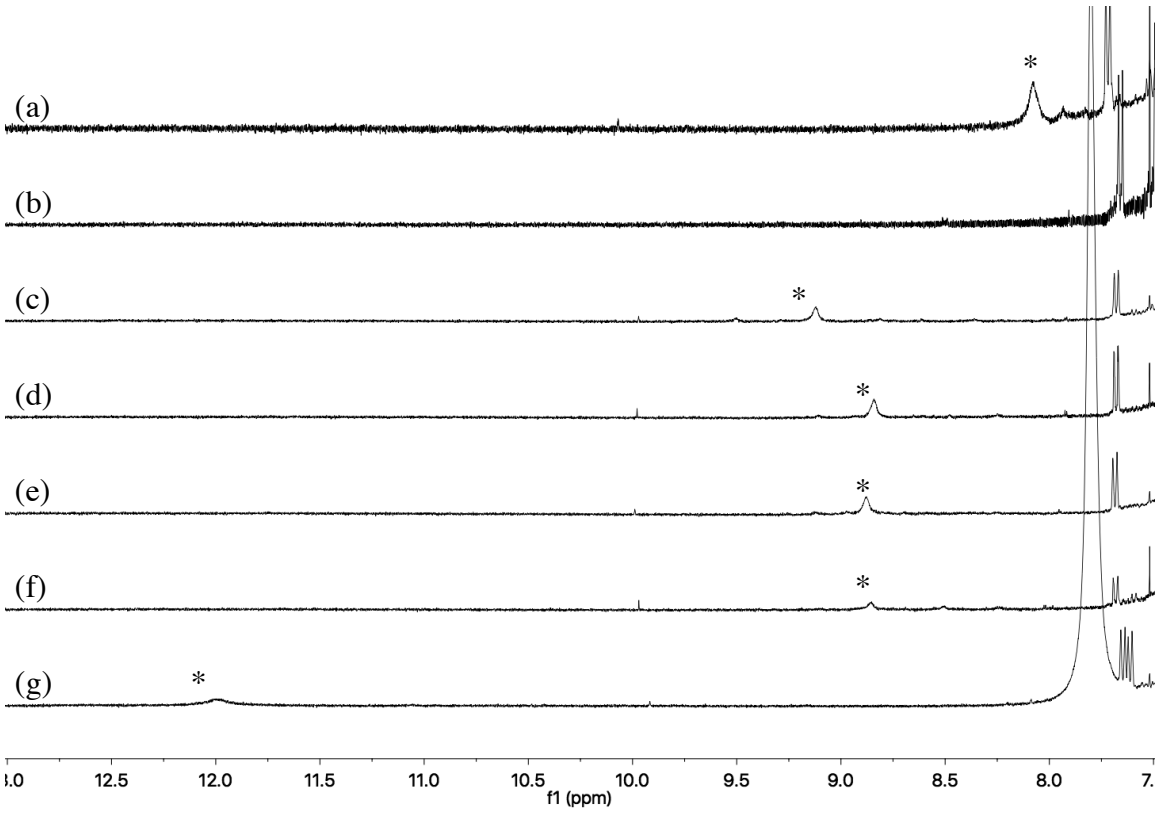


Figure 2.1: Partial ^{1}H NMR spectra (400 MHz) recorded in chloroform-*d*: (a) the reaction mixture of Scheme 2.2; (b) this reaction mixture + 10 equiv F^-; (c) this reaction mixture + 10 equiv Cl^-; (d) this reaction mixture + 10 equiv Br^-; (e) this reaction mixture + 10 equiv NO_3^-; (f) this reaction mixture + 10 equiv HSO_4^-; (g) the reaction mixture + 10 equiv $H_2PO_4^-$. All anions were studied as their tetrabutylammonium salts. * designates the possible N-H signal of the indole moiety.

2.4 Experimental Details

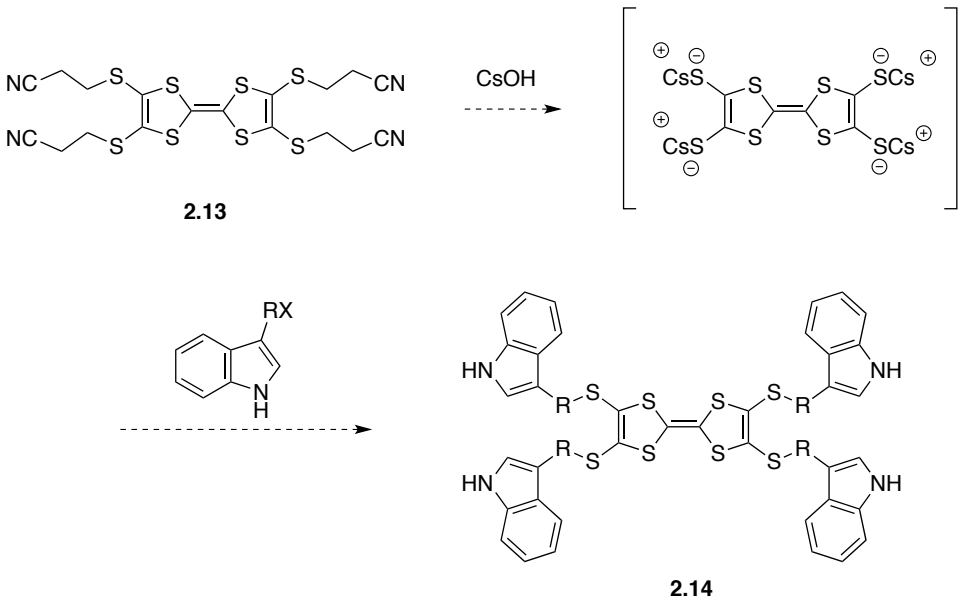
Compound 2.12

Bis(tetrabutylammonium) bis(1,3-dithiole-2-thione-4,5-dithiolato)zinc complex (0.93 g, 1.0 mmol) and **2.11** (1.2 g, 3.9 mmol) were dissolved in 100 mL of acetonitrile and heated at reflux for 4 h. After removal of the volatile solvent under reduced pressure, the residue was redissolved in 200 mL of methylene chloride. The resulting solution was washed with water (3 X 200 mL). The organic phase was separated off and dried over Na_2SO_4. After concentrating by rotorary evaporator, the residue was purified via column chromatography over silica gel (eluent hexanes:ethyl acetate = 4:1, R_f = 0.5) to yield this product as a yellow solid (1.23 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J = 15.0 Hz, 1H), 7.87 (d, J = 14.9 Hz, 2H), 7.50 (t, J = 11.9 Hz, 2H), 7.44 (t, J = 10.0 Hz, 2H), 7.40 (s, 1H), 7.37 (t, J = 10.0 Hz, 1H), 7.28 (t, J = 11.0 Hz,1H), 3.78 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.3, 138.04, 137.8, 135.3, 134.3, 129.6, 129.3, 126.9, 125.6, 125.2, 123.6, 119.8, 117.0, 113.9, 31.8 ppm. HR ESI MS calc. m/z for $C_{33}H_{24}N_2O_4S_7$ $(M+Na)^+$ 758.96730; obs. m/z 758.96710.

2.5 Conclusions and Future Work

In summary, the synthesis of a new receptor **2.10** was attempted. This target was designed to contain an anion-recognizing indole moiety and to provide a new approach to create a potential optical/electrochemical dual signaling anion sensor. Unfortunately, this target compound could not be obtained due to synthetic difficulties. From what was observed, it is suspected that the undesired decomposition reflects the harsh reaction

conditions need to effect phosphorus-mediated coupling. As the coupling reaction is critical to synthesis of TTF derivatives, an alternative synthetic method will be need if 2.10 is to be occurred. One approach could involve fusing indole derivatives to a preformed-TTF core, as suggested in Scheme 2.2. This represents a strategy employed recently Salle et al.[14] to obtain a different set of substituted TTF derivatives.



Scheme 2.2: Proposed synthetic pathway to accomplish the desired synthesis.

Chapter 3: Redox- and pH-Responsive Orthogonal Supramolecular Self-Assembly: Creation of an Ensemble Displaying Molecular Switching

3.1 Introduction

This chapter represents the author's contribution to a project initiated by former group member, Dong Sub Kim. This effort was part of responding to reviewers for a manuscript that has been resubmitted to JACS but not yet accepted or rejected definitively. The first section of the chapter is designed to put this contribution in context.

3.1.1 Self-assembled Materials

A longstanding goal in the chemical community is to create complex systems that can be precisely controlled via the application of an external stimulus. Such control is attractive in the rise of functional materials that are adaptive to the external environment. These systems have already showed promise in the development of various drug delivery systems,[1,2] as well as self-healing materials.[3,4]

Molecular approaches based on supramolecular motifs have been widely used to construct systems that respond to light,[5] heat,[6] ions or small molecules.[7-9] Among the underlying non-covalent interactions that have been exploited are hydrogen bonding and metal-ligand interactions. The use of such orthogonal interactions has an advantage in that it usually provides systems that are is more predictable in the context of self-assembly. It also allows a greater number of external stimuli to be used in the systematic control of the associated responsive materials. The remarkable complexitiy of biological systems are examples of exceptional utilization of orthogonal interactions.[10]

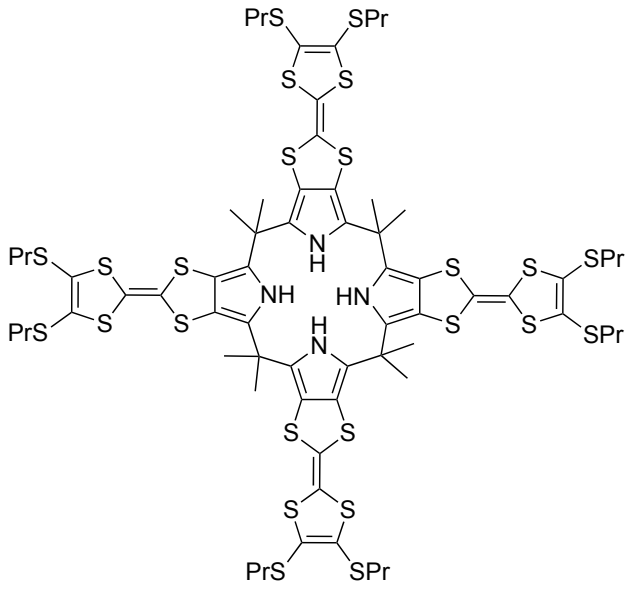
3.1.2 Tetrathiafulvalene-substituted Calix[4]pyrroles

In the absence of a bound anion or solvent, calix[4]pyrroles adopt the more thermodynamically stable 1,3-alternate conformation. However, when a coordinating anion is present, calix[4]pyrroles undergo conformational change and adopts the anion-bound cone form.[11] A calix[4]pyrrole with four tetrathiafulvalene (TTF) subunits was first synthesized by Nielson in 2004.[12] Later, Fukuzumi and Sessler reported the formation of TTF-annulated calix[4]pyrroles with various fullerene guests and noted their ability to undergo a variety of anion- and cation-driven molecular switching processes. For instance, it was noted that with these TTF-annulated calix[4]pyrroles, a conformational change triggered by anion binding to create the bowl-like pocket into which a variety of complexes with electron deficient guests can be formed. Electron deficient substrates tested included an imidazoliumquinone,[13] Li@C_{60},[14] C_{60}, and C_{70}.[15] These complexes were stabilized via charge-transfer complex both in solution and in the solid states. This could then be decomposed by switching the calix[4]pyrrole conformation or by competition with other electron deficient guests.

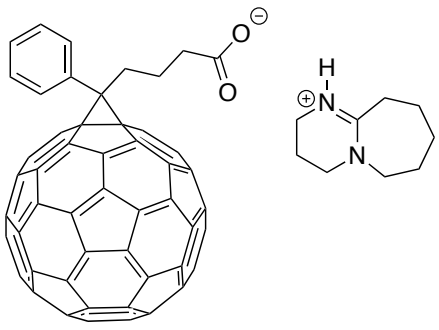
A system with control over multiple addressable states was constructed by former group member Dong Sub Kim. He used a tetra-substituted TTF calix[4]pyrrole in concert with a bis-pyridinium calixp[4]pyrrole. Interconversion between a 1:1 self-assembled oligomer, a 2:1 capsule, and the corresponding monomers (i.e., three separate states) could be controlled via the binding of specific combinations of cation and/or anion. The system was able to display a NAND logic gate behavior without the need to invoke mechanical or covalent bonds.[16]

3.2 DESIGN OF THE SYSTEM AND STRATEGY

Multiple self-assembled systems have been described in the literature that rely on orthogonal noncovalent interactions. However, there has been no report of oligomeric constructs composed of stimuli-responsive heteroditopic monomers. It is expected that the higher level of stimulus-based control provided by using switchable monomers will lead to new classes of responsive materials. To test this possibility, a system that relies on tetrathiafulvalene-annulated calix[4]pyrrole (TTF-C4P), **3.1**, used in conjunction with a ditopic substrate, **3.2**.



3.1



3.2

The ditopic substrate chosen for use is the anion of phenyl C_{61} butyric acid (**3.2**). This carboxylate was expected to interact with **3.1** and induce a conformational change. This change was expected to create a bowl-like cavity into which the fullerene subunit

present in **3.2** can bind via charge-transfer interactions. To the extent it occurs, it would generate an oligomeric construct. In principle, the formation of oligomer can be reversed by increasing the pH to regenerate the carboxylic acid, releasing **3.2** from **3.1**. On the other hand, the decomposition of the oligomeric construct can also in principle be achieved via redox processes that exploit the redox active TTF and fullerene subunits. Specifically, it was expected that the oxidation of the TTF moiety would will cause the **3.1** to lose its ability to bind the electron-poor fullerene subunit present in **3.2**. This would trigger deoligomerization.

The systematic design of this system and preliminary studies were carried out by previous group members. The initial results were written up and submitted for publication. I joined the project after the submitted paper was returned for revision. I thus contributed only the synthesis of components **3.1** and **3.2**, which I re-prepared, and the study of pH-responsive oligomerization and deoligomerization.

3.3 Result and Discussion

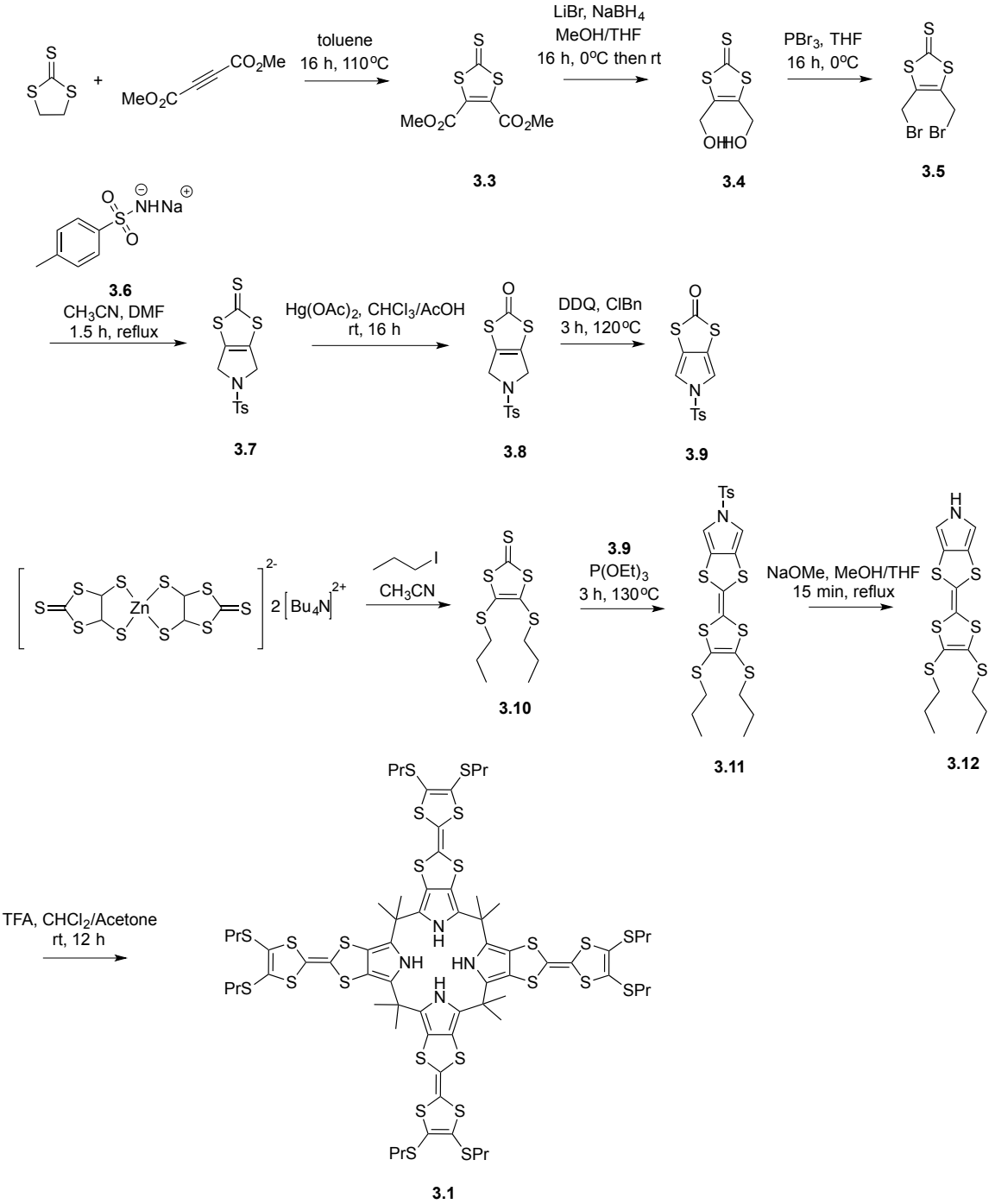
As noted above, my contribution to this projected was limited. I was responsible only for the synthesis of components **3.1** and **3.2** and the study of pH-responsive oligomerization and deoligomerization.

3.3.1 Synthesis and Characterization of the Compounds

Compound **3.1** was synthesized following the synthetic route shown in Scheme 3.1.

The reaction conditions from the previous report[13] were optimized for the synthesis. The characterization data for the final product matched that reported in the literature.[13]

The protonated form of compound **3.2** was synthesized by subjecting commercially available phenyl C_{61} butyric methyl ester to hydrolysis with hydrochloric acid and acetic acid. The reaction conditions were adopted from the literature, and product gave characterization data that matched that reported the data in the literature.[16] The deprotonated form, salt **3.2**, was prepared *in situ* by adding 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).



Scheme 3.1: Optimized synthesis of **3.1**.

3.3.2 Spectroscopic Studies

2D ^{1}H DOSY NMR spectroscopic experiments were conducted to ascertain whether oligomeric species were obtained upon mixing **3.1** and **3.2** and whether this putative formation could be controlled via the addition of base and acid. As described in a previous section, it was expected that the presumed anion-triggered oligomerization could be induced upon the addition of base (DBU) to produce **3.2** *in situ* from its conjugate acid. Exposure of the resulting oligomer, if formed, to acid (MSA, methanesulfonic acid) was then expected to protonate **3.2** and trigger disassociation. Such acid-base switching on and off of the presumed oligomerization process could be monitored possibly by noting changes in the diffusion coefficients as a function of conditions. To test this idea, the diffusion coefficients (D) corresponding to the peaks of the meso-methyl protons of **3.1** and the aromatic protons on phenyl group of **3.2** were determined by DOSY spectra in the presence of base and acid. The DOSY experiment was conducted by mixing **3.1** and **3.2** in dichloromethane with first DBU then MSA. The resulting DOSY spectra are shown in Figure 3.1 below.

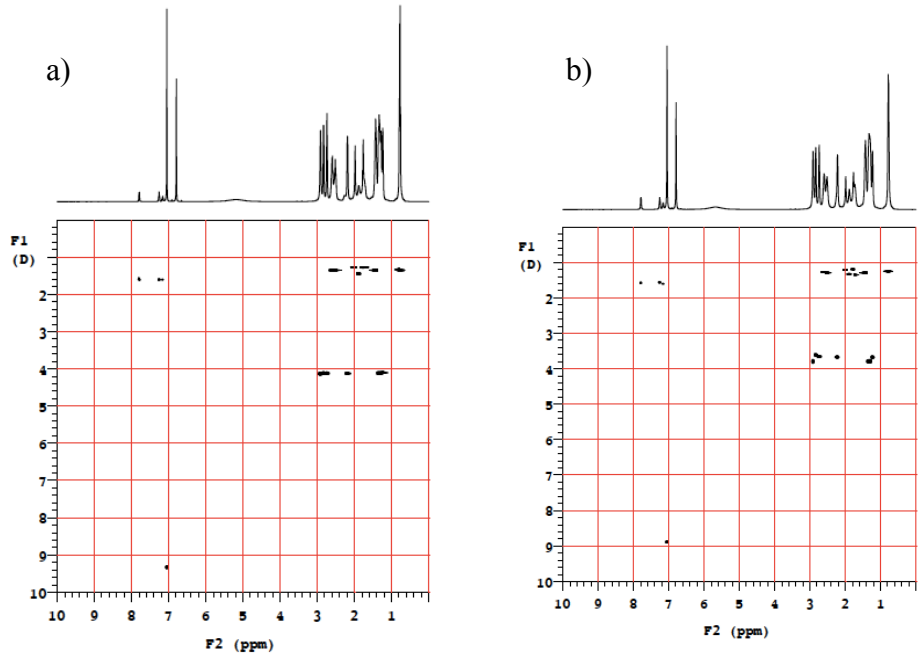


Figure 3.1: ^{1}H DOSY NMR spectra of a) **3.1** (10 mM) + **3.2** (10 mM) + DBU (3 equiv) in 1,2-dichlorobenzene-d_4; b) **3.1** (10 mM) + **3.2** (10 mM) + **DBU** (3 equiv) + MSA (3 equiv) in 1,2-dichlorobenzene-d_4.

It was also predicted that such oligomerization would be affected by the concentration of each monomer present in the sample. It is likely that a greater level of oligomerization will occur when each monomer (**3.1** and **3.2**) is present at a higher initial concentration. To test this hypothesis, the diffusion coefficients corresponding to the peaks of interest were monitored as a function of total concentration while the ratio of **3.1** and **3.2**, and DBU was held constant at 1:1:3. As can be seen from an inspection of Figure 3.2, the expected decrease in D value was seen as the concentraiton of all components was increased.

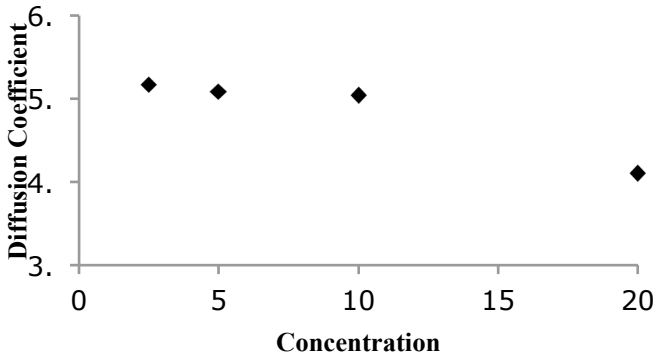


Figure 3.2: Plot of concentration of **3.1** + **3.2** in 1:1 ratio in mM vs. diffusion coefficient (10^{-10} m^2/s) for proton signals of interest. DBU was present in all samples at 3 molar equivalents.

3.4 CONCLUSION

In this chapter, the author's contribution to the preparation and study of a supramolecular oligomeric material based on a TTF-annulated calix[4]pyrrole and a fullerene derivative bearing a carboxylate anion moiety are described. Both components were synthesized via now optimized synthetic pathways. Evidence for the switching "on" and "off" of oligomerization as a function of base and acid was obtained from ^{1}H DOSY NMR spectroscopic analyses. Similar studies were carried out as a function of total component concentration. Combined with additional data from light scattering and electrochemical analyses (not the author's work), a case was made for the rationally designed creation of a highly orthogonal system that could be controlled by several kinds of external stimuli.

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